Some problems of correcting the zero-point energy problem in classical trajectories

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We have examined the effects on the fundamental behavior of the dynamics of applying constraints to control the aphysical flow of zero-point energy in classical trajectories of molecular systems. Test calculations on the popular Hénon-Heiles potential surface show that these constraints can induce physically undesirable effects in the dynamics, e.g., changing quasiperiodic motion (characterized by a few discrete frequencies) into chaotic motion (characterized by a continuous distribution of frequencies).

1. Introduction

Classical trajectories have been, and continue to be, crucial in the evolution of our understanding of chemical dynamics. Classical simulations are feasible for many problems where quantum treatments are not and, fortunately, many chemical processes occur under conditions where the classical approximation is valid. However, we are still faced with the fact that real systems are quantum mechanical and there are many situations where classical trajectories fail. One such problem is the failure of classical mechanics to preserve zero-point energy constraints. Various approaches have been tried to correct this problem [1–6]. We raise the question of whether it is possible to “fix” the zero-point energy problem without altering the dynamics such that equally or more serious aphysical behavior is introduced.

Some studies have been done to determine the contribution of the zero-point energy to reaction rates in classical studies by including only a fraction of the

zero-point energy of the molecule [1,2]. Guan et al. [1] used this approach in studies of the near-threshold overtone-excitation-induced photodissociation of H₂O₂. In their calculations, zero-point energy combined with excitation of an OH local mode to $\nu_{\text{OH}}=5$ resulted in a total energy in excess of the barrier to O–O bond fission. However, excitation of $\nu_{\text{OH}}=5$ alone provides insufficient energy to traverse the barrier (*thermally assisted*, single-photon overtone-induced photodissociation experiments pumping $\nu_{\text{OH}}=5$ have been performed by Crim and co-workers [7]). Guan et al. found that there was a significant dependence of the classically calculated dissociation rates on the amount of zero-point energy. However, they found that mode-specific effects are qualitatively the same for various amount of zero-point energy: That is, various internal distributions of energy in excess of the “zero-point level” yield qualitatively similar behavior as the fraction of the zero-point energy is varied.

Lu and Hase [2] studied the effect of zero-point energy in calculations of the linewidth of C–H overtones following excitation of a C–H local mode in benzene. They considered cases in which they added a fraction of the zero-point energy ($0 \leq f_{\text{zpe}} \leq 1$) to the modes of the system and in which they excluded

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zero-point energy from selected normal modes. The calculated linewidth was less than 1.0 cm^{-1} for $f_{\text{zpe}}=0$, regardless of which overtone state was sampled. Using $f_{\text{zpe}}=0.04$ gave results in good agreement with experiments for the $n=3$ state. Larger values of f_{zpe} yielded linewidths an order of magnitude larger than experimental values. They found that excluding zero-point energy from seven normal modes having strong CCH bend character (with zero-point energy in the 14 remaining modes) had a significant effect on the linewidth, decreasing the value by a factor of 3 to 5 (relative to results obtained with all zero-point energy present), depending on which overtone was excited. By contrast, excluding zero-point energy from the other 14 normal modes but adding it to the seven CCH modes gave results in near agreement with the full-ZPE case, except for higher overtone excitations. Lu and Hase suggest that one promising way to assign "zero-point energy" is to use the Wigner distribution as a means of selecting initial energies for unexcited modes since it is theoretically based and leads to a most probable classical "zero-point energy" of zero.

Lu and Hase [3] also considered the effects of decreasing the number of degrees of freedom in the system in an effort to reduce the effects of aphysical classical energy flow. In particular, they extracted portions of the force field for the planar benzene molecule (C_6H_6) to yield force fields for two fragments (C_3H and C_3H_3) and compared linewidths for the two fragments with experimental measurements. The effect of doing so was to decrease the total energy content of the system and change the intramolecular couplings. They found that the overtone linewidths in the fragments were in considerably better agreement with the experimental measurements for benzene excited to the corresponding state.

Another possible route to understanding the effects of zero-point energy flow in classical trajectory calculations is illustrated by the work of Nyman and Davidsson [4] on the exchange reaction $\text{O}(^3\text{P}) + \text{OH}(^2\Pi) \rightarrow \text{O}_2(^3\Sigma_g^-) + \text{H}(^2\text{S})$. They started with "all-or-none" of the zero-point energy in the $\text{OH}(^2\Pi)$ vibration, and then selectively "threw out" trajectories which did not satisfy predefined criteria regarding zero-point energy in the reaction products ($\text{O}_2(^3\Sigma_g^-)$ or, in the case of unreactive scattering, $\text{OH}(^2\Pi)$). The criteria range from retaining all tra-

jectories regardless of the final vibrational energy to retaining only those trajectories that had at least the zero-point energy. The results showed a strong dependence on which scheme of categorizing the trajectories is employed: The treatment that yields the best agreement between the calculated and experimental results depends upon what properties are being compared.

These examples serve to exemplify "passive" methods for dealing with the zero-point energy problem and also illustrate the effects of zero-point energy flow. They are based on the idea of allowing the trajectories to evolve according to the classical equations of motion. By contrast, an "active" method for controlling the flow of zero-point energy during the course of individual trajectories has been proposed simultaneously by Bowman, Gazdy, and Sun [5] and Miller, Hase, and Darling [6]. The approach by Bowman et al. is encompassed in that of Miller et al. The gist of both methods is that, so long as none of the (assumed separable) mode energies in a system fall below the zero-point level, it should be allowed to evolve according to the classical equations of motion. However, when one or more of the mode energies falls below the zero-point, an instantaneous, external force is applied so as to exactly reverse the velocity in the mode(s) in which the energy has dropped below the zero-point level. If the kinetic energy is diagonal, then the total energy will be conserved. (However, the angular momentum will not be conserved except in special cases such as linear systems.)

Bowman et al. [5] used the Hénon-Heiles [8] Hamiltonian to show that regions of phase space corresponding to individual mode energies having less than zero-point energy are, in fact, unavailable to trajectories in which the momentum reversal constraint is applied. Miller et al. [6] considered a general treatment more germane to "real" systems. They proposed that, for sufficiently small energies, one can use the equilibrium normal modes as a basis for determining whether a particular mode is in a state consistent with the zero-point energy requirement: That is, a trajectory can be computed in Cartesian phase space and the vibrational normal-mode energies (based on the equilibrium geometry of the molecule) monitored until the energy of a mode falls below the corresponding zero-point level and then the

velocity of that normal mode is reversed. A new set of Cartesian momenta are obtained by back transformation and the trajectory is continued. They applied this algorithm to a collinear HC₄ "molecule".

Miller et al. [6] further generalized their method to deal with zero-point energy in highly excited (e.g., reactive) systems. The more general version is quite similar to the simple approach except that, rather than computing the normal-mode energies using the equilibrium Cartesian coordinates as a basis, the instantaneous normal modes at configuration $q(t)$ are computed at each step of the trajectory and used as a basis for determining the instantaneous zero-point energy.

The point we address here is whether or not it is feasible to employ "active" constraints to deal with the zero-point energy problem. To this end we apply the methods suggested by Bowman et al. [5] and Miller et al. [6] to the simplest situation one can imagine, the dynamics of the ground state of a system of coupled oscillators (specifically, the Hénon–Heiles Hamiltonian). The results given by the usual, i.e. unconstrained classical mechanics and by the zero-point energy constrained classical mechanics are compared to the correct quantum-mechanical calculation of several quantities of interest.

2. Model and methods

The model is the much-used Hénon–Heiles [8] Hamiltonian for two coupled oscillators, given in reduced units ($m = \omega_x = \omega_y = 1$)

$$V(x, y) = \frac{1}{2}(p_x^2 + p_y^2 + x^2 + y^2) + x^2y - \frac{1}{3}y^3. \quad (1)$$

We also considered cases with $\omega_x \neq \omega_y$, but the qualitative behavior and general conclusions were similar to those below, so we focus on this particular case.

Initial conditions for all the trajectory calculations were selected in the usual quasiclassical fashion [9] to correspond to the ground state of the zeroth-order (harmonic) potential

$$V_0(x, y) = \frac{1}{2}(x^2 + y^2) \quad (2)$$

i.e.

$$x_0 = \sqrt{(2n_x + 1)\hbar} \cos q_x,$$

$$\begin{aligned} p_{x0} &= -\sqrt{(2n_x + 1)\hbar} \sin q_x, \\ y_0 &= \sqrt{(2n_y + 1)\hbar} \cos q_y, \\ p_{y0} &= -\sqrt{(2n_y + 1)\hbar} \sin q_y, \end{aligned} \quad (3)$$

where q_x and q_y were selected randomly in the interval $(0, 2\pi)$ and $n_x = n_y = 0$. Here $\hbar$ is a reduced dimensionless Planck's constant which determines how quantum-like the system is; for the results given below it was chosen as $1/7\pi$, though other values were also explored. For the constrained dynamics calculations, we used the "more general" version of the method of Miller et al. [6] which applies the zero-point energy constraint instantaneously (i.e. at each step of the trajectory) to a local harmonic estimate of the zero-point energy of each mode.

We monitored the time dependence of two quantities of interest in order to assess the validity of the classical calculations (unconstrained and constrained), namely the harmonic mode energies

$$E_i(t) = \frac{1}{2}(p_i^2 + q_i^2), \quad (4)$$

for $i = x$ and y , and also the autocorrelation functions of the two coordinates

$$C_i(t) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt' q_i(t') q_i(t' + t), \quad (5)$$

also for $i = x$ and y . (In practice it is actually more informative to look at the power spectra $I_i(\omega)$, the Fourier transform of the time correlation functions, and this is what is considered in section 3 below.) Both quantities, eqs. (4) and (5), were averaged over the initial phases of the two modes (cf. eq. (3)) using ensembles of 100 trajectories.

For comparison with the two classical calculations, quantum-mechanical values of the above quantities were also computed. The energy in mode i (cf. eq. (4)) is given quantum mechanically by

$$E_i(t) = \langle \phi_0 | \exp(iHt/\hbar) h_i \exp(iHt/\hbar) | \phi_0 \rangle, \quad (6a)$$

where $\phi_0(x, y)$ is the initial zeroth-order (ground state) harmonic oscillator wavefunction, and h_i is the harmonic oscillator Hamiltonian for mode i ,

$$h_i = \frac{1}{2}(p_i^2 + q_i^2). \quad (6b)$$

If $\{\Psi_k\}$ and $\{E_k\}$ are the eigenfunctions and eigen-

values of the total Hamiltonian H – obtained by diagonalizing the matrix of H in a sufficiently large harmonic oscillator basis – then the time evolution operator in eq. (6a) can be expressed as

$$\exp(-iHt/\hbar) = \sum |\Psi_k\rangle \langle \Psi_k| \exp(-iE_k t/\hbar), \quad (7)$$

so that eq. (6a) becomes

$$E_i(t) = \sum_{k,k'} \langle \phi_0 | \Psi_k \rangle \exp[i(E_k - E_{k'})t/\hbar] \times \langle \Psi_k | h_i | \Psi_{k'} \rangle \langle \Psi_{k'} | \phi_0 \rangle. \quad (6c)$$

Similarly, the time correlation function is given quantum mechanically by

$$C_i(t) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt' \langle \phi_0 | \exp(iHt'/\hbar) \times g_i \exp(-iHt'/\hbar) \exp[iH(t+t')/\hbar] g_i \times \exp[-iH(t+t')/\hbar] | \phi_0 \rangle, \quad (8a)$$

and again using eq. (7) for the time evolution operators, this becomes

$$C_i(t) = \sum_{k,k'} |\langle \phi_0 | \Psi_k \rangle|^2 |\langle \Psi_k | g_i | \Psi_{k'} \rangle|^2 \times \exp[i(E_k - E_{k'})t/\hbar]. \quad (8b)$$

The time dependence of the zeroth-order mode energies, eqs. (4) and (6), exhibit time dependence only because the initial state is not the true ground state. This is most obvious in the quantum case, eq. (6), which would be time-independent if $|\phi_0\rangle = |\Psi_0\rangle$. (Expectation values of all operators are constant in an eigenstate.) The time correlation functions, eqs. (5) and (8), however, exhibit time dependence even if the initial state is the true ground state.

3. Results and discussion

Fig. 1 shows the harmonic mode energies for the unconstrained (fig. 1a) and constrained (fig. 1b) classical calculations and for the quantum calculation (fig. 1c). The results of the constrained classical mechanics are perhaps in somewhat better agreement with the quantum results, but the unconstrained classical are not in serious error. That is, for

Fig. 1. Time-dependent harmonic mode energies for the unconstrained and constrained classical mechanics (panels (a) and (b), respectively), and for the quantum-mechanical calculation (panel (c)). The results are for the "ground state" of the Hamiltonian with $\hbar = 1/7\pi$. The classical results are averages of 100 trajectories.

this situation here is really no zero-point energy "problem".

Fig. 2 shows the results for the power spectra, the

Fig. 2. Power spectrum of the "ground state" dynamics. Panels (a) and (b) are for the unconstrained and constrained, respectively, classical mechanics. Quantum results are shown in panel (c).

Fourier transform of the time correlation functions. Here matters are quite different. The normal, i.e. unconstrained, classical mechanics gives a single peak at $\omega \approx 1$, signifying quasiperiodic motion. (Fig. 3a shows the coordinate space projection of this trajectory, confirming this.) The constrained classical mechanics, however, shows a broad, essentially continuous distribution of frequencies, characteristic of chaotic dynamics. (Fig. 3b shows the configuration space projection of a constrained trajectory, confirming the chaotic behavior of the motion.) The quantum result in fig. 2c is clearly much closer to that

Fig. 3. Configuration-space projections of representative unconstrained and constrained (panels (a) and (b), respectively) classical trajectories.

of the *unconstrained* classical dynamics. The zero-point energy constraints thus severely modify the classical dynamics, in a physically incorrect fashion.

A variety of other initial conditions and potential parameters were considered [10], as well as other versions of the zero-point constraint model, but the qualitative results were all similar to those above. The constrained dynamics does indeed prevent the energy in each degree of freedom from falling below its local zero-point value, but the "harshness" of the constraint is too severe, inducing chaotic behavior into the dynamics in cases for which one does not believe this to be physically correct.

4. Concluding remarks

For the example treated in this paper, a system of coupled oscillators initially in its (approximate) ground state, there is no zero-point energy problem. (Note, though, that sometimes the classical mechanics is chaotic at an energy corresponding to the zero-point energy [11].) It is thus disappointing that the proposed model for correcting problems with zero-point energy does not describe this situation well. The problem seems to be that the "hard wall" character of the constraint is too harsh, inducing chaotic behavior in the dynamics. Perhaps a "kinder, gentler" version of the model can be devised (e.g., a soft repulsive interaction in the action variable), but it remains to be seen whether any strictly classical "fix" can be successful and useful.

One may, of course, decide to give up on a strictly classical approach and try to utilize various semiclassical approximations. Alimi et al. [12] have recently suggested an approximate version of Heller's [13] semiclassical wavepacket methods for this purpose. This is a promising approach and certainly worth pursuing, though one notes that it involves more effort to apply than does a purely classical treatment (e.g., matrix elements of the potential en-

ergy surface must be computed), and Gaussian wavepackets can give unphysical results in very anharmonic systems.

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